

## PYROLYSIS OF BIOMASS AND POLYMER MIXTURES - MUNICIPAL SOLID WASTE AS AN EXAMPLE

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### ABSTRACT

Incineration and thermal conversion of municipal solid waste are receiving considerable attention from both a political and scientific viewpoint. Polymers are present, both natural and manmade, representing about 80 weight % of the waste. Little quantitative reaction data is available and potential pollution problems have been identified when the polymeric mixtures contain chlorine and are reacted or incinerated at high temperature. The purpose of this work is to provide a quantitative basis for the engineering design of reactors to recover hydrocarbons from this waste. We have performed experiments under controlled conditions on a reasonably well-characterized "model" for municipal solid waste, that is, commercially available densified refuse-derived fuel (d-RDF), made by sorting, drying and compressing municipal solid waste. The resulting relatively uniform composition and density pellets have, however, low thermal conductivity, making the apparent reaction rate limited by the local heat transfer rate. This pyrolysis study employs single, "macro"-particle experiments where particle non-isothermality can be measured and its effect on product slate can be understood. A variety of polymeric substrates as well as commercial RDF have been heated under well-controlled conditions spanning those of industrial importance. The devolatilization behavior, such as time-temperature history and evolved gas composition, has been measured in detail. The results have been used to develop correlations applicable to reactor design and pollution control. Specialized statistical methods are used to quantify the contribution of a single mixture constituent to pyrolysis behavior. Conclusions from the experiments have aided in the development of a mathematical model of the devolatilization process and have increased our understanding of the role of reactant composition, as well as particle mass and heat transfer, during gasification and combustion.

### INTRODUCTION

The ongoing work described in this preprint is a portion of a study (1) of the transport rates and chemical reaction behavior during thermal conversion of a particular form of municipal solid waste (MSW), namely densified refuse-derived fuel (d-RDF). It is made commercially by removing recyclables and non-combustibles, drying and compressing the remaining mixture (manmade and natural polymers as well as other materials) into pellets of relatively uniform size and density (~1-2 cm diameter, 2-3 cm long cylinders, specific gravity between 1 and 2). The resulting material is considerably more compact, has approximately the heating value of coal, and can be economically transported to a central site for thermal conversion. It is envisaged that this central site could then be expected to have a larger, more advanced design thermal conversion process with potentially the flexibility to optimize certain products, and certainly the capability of pollution control and monitoring.

While some work has been performed on d-RDF and MSW (1-3), it remains to be determined what reaction conditions optimize particular products, what are the effects of pellet moisture, size and density on conversion rate and products, and in particular, what changes in the waste stream polymeric mixture result in desirable or undesirable pyrolysis products. Reactor design will require devolatilization kinetics data on the d-RDF constituents, and a knowledge of whether constituents co-react when confined to the interior of the relatively non-porous particle of d-RDF, or whether the constituents react independently. By studying the behavior of single particles as in other studies (4), we can direct the efforts in mathematical modeling of the pellet behavior, provide a basis for judging adequate kinetic models, and make suggestions regarding appropriate reactor configurations.

### EXPERIMENTAL ASPECTS

The experimental apparatus consists of a single particle reactor which allows determination of particle temperature and gas evolution history, heat transfer rates, and total product analysis. It is described elsewhere (1,5). The d-RDF compositions studied span the range found in practice (Table 1) as interpreted by the standard deviation of the 10 composition studies available in the recent literature. To

understand the role of composition, laboratory-fabricated pellets as well as commercial pellets are studied under the well-controlled reaction conditions likely to occur in industrial practice (Table 2).

As in other studies where sample size must remain constant while composition is changed, in this study the weight fractions of waste constituents sum to unity, making the composition variables correlated and the interpretation of results ambiguous unless special experimental designs and biased regression methods are employed. Consider a 1 gram sample of say 4 equal concentration components (25% by weight). Its reaction behavior is to be compared to another 1 gram sample (so sample temperature history remains constant) with a different composition. In the second sample, it is desired to determine the pyrolysis product slate change when one of the constituents is reduced to say 10% by weight. Owing to the constant sample size, this change necessitates that one of the other constituents make up the remaining 15%. Changes in behavior cannot be unambiguously attributed to a reduction in the former, but rather to either a reduction in the former or increase in the latter constituent. This difficulty is lessened when one constituent predominates as in the case of paper-like components of MSW. In Table 1 it can be seen that components 1-4, 7, and perhaps 6 can be approximated by paper such as newsprint with a lignin content close to that of native wood. Daugherty et al. (6) have studied the stability of d-RDF with respect to biological degradation and long term integrity of the pellets. They found a well-behaved d-RDF pellet can be made when  $\text{Ca}(\text{OH})_2$  is used as a binder comprising approximately 1-8% by weight. The binder is similar to the inorganic material that accompanies the combustible fraction in actual MSW. For a number of reasons (1), we were able to justify reducing the composition classes in d-RDF to four: paper as exemplified by newsprint, plastics as equal fractions PVC and polyethylene, non-combustibles as exemplified by metal and glass, and inorganic substances as exemplified by binder. The ranges over which these four components were varied are shown in Table 2. The combination of compositions and reaction conditions actually run in our experimental program was a special mixture design (1,7), and ridge regression as well as other biased regression methods were used to calculate the effects of composition changes.

The procedure consists of heating the sample one-dimensionally with a constant radiative heat flux for a fixed pyrolysis time of 12 min. The constant heating time can be rationalized as analogous to the constant time-at-temperature (residence time) a particle experiences in a moving bed reactor. Particle size is varied as are initial particle moisture, composition, and the intensity of the heat flux, all in systematic combinations dictated by the experimental design (1,7). During the pyrolysis, time-temperature profiles are measured at several depths (Fig. 1) and gas evolution rate and composition are also measured as functions of time (Fig. 2). Hydrocarbons are measured as well though only carbon oxides and total gas yield are shown in Fig. 2. The overall pyrolysis product yields are measured as integrated batch yields as well; Table 3 reports typical yields of interest for this paper. In addition, though not the subject of this paper, tar composition is measured in detail as are char surface area and composition by FTIR. To narrow the focus, this paper will concentrate on the composition history of the gases since it is seen to be an indicator of the pyrolysis chemistry occurring in the large, non-uniform temperature particle. The gas composition is measured semi-continuously using a computer controlled automatic sampling valve and a gas chromatograph.

## RESULTS

The d-RDF pellets were pyrolyzed and the time-temperature histories (at 2, 6 and 9 mm into the particle) and gas flux histories are shown in Figs. 1 and 2 respectively. A temperature plateau at about 100°C can be seen to occur at interior thermocouple locations owing to the constant temperature evaporation of water as the heating front passes. The gases are released (Fig. 2) with the peak in the rate controlled by the heating rate applied at the surface, as well as the size and moisture content of the particle. Using data similar to Fig. 2, this paper will present a limited discussion on the comparison of pyrolysis behavior between d-RDF samples with high and low fractions of plastics.

Direct comparisons will be presented in which the only difference between 2 experiments is the fraction of plastics (the remainder being made up by paper (newsprint)). In these, it is useful to *subtract* the yields, or subtract the gas flux histories and report the difference as a function of time. That is, the data analogous to Fig. 2 for an experiment with low fraction plastics are subtracted from the data resulting when a high fraction plastics pellet is pyrolyzed. The *fractional* difference provides perhaps more insight when concentrations are small as in our pyrolyses, and this is shown in Figs. 3 and 4 for carbon oxides and hydrocarbons respectively (the low plastics result is the reference or denominator). Thus Figs. 3 and 4 report fractional difference in gas composition as a function of pyrolysis (reaction) time for the cases of high and low plastics content in d-RDF. It is important to keep in mind the sample-to-

sample variation expected in such a heterogeneous reactant and we have studied this by replicate experiments. For replicates, the difference between measured gas concentrations expressed as a fraction of one of them is less than approximately two-fold over the entire time interval; thus fractional concentration variations greater than 3 in Figs. 3 and 4 represent probable composition effects in the pyrolysis behavior. It can be seen that the hydrocarbons, especially  $C_2H_4$  and  $CH_4$ , appear to be sensitive to the concentration of plastics. This is to be expected judging from the thermal degradation products measured for polymers (8-16).

The time-dependent pyrolysis behavior is to likely represent data with a high degree of noise or uncertainty in them. A more robust measurement, though revealing less kinetic and reaction information, is the comparison of overall (time-integrated) yields from a plastics-rich compared to a plastics-poor sample of d-RDF. In Table 4 are presented three direct comparisons of overall yields, and as before, the pyrolysis component concentrations in the product gas are subtracted for the two cases, and the result expressed as a fractional difference. The three direct comparisons represent different values of other experimental conditions. It can be seen in Table 3 that even replicate d-RDF (laboratory fabricated) pyrolyses exhibit variations in measured product concentrations of about 20%. Thus only differences in overall yields exceeding 25-30% in columns 5,9, and 13 (Table 4) can be interpreted as actual composition effects attributable to the high plastics content. This high a difference is observed for all gases except  $CO_2$ , and in some cases such as ethylene, the difference is over a 200% increase in yield in the product.

## DISCUSSION

The composition effects presented here are direct comparison experiments, that is, only one pair of compositions is varied at a time. Other data (1) indicate that the magnitude of these enhanced pyrolysis product yields is dependent in a complex way on all the other reaction condition variables, namely particle size, initial moisture, heating rate experienced, and in particular, on the amount of inorganic material (binder) present. It is interesting to note that the experimentation to date, and the regression of the results indicate that the d-RDF constituents can be assumed to react independently. Current work is focused on mathematical modeling of the independent reactions, prediction of the effect of such a high moisture content as is typical of MSW (Table 1) and prediction of the coupled processes of heat transfer and reaction rate in the non-isothermal RDF particle.

### Comparison to Pyrolysis of Polymers

It is well known that thermal degradation of Poly(vinyl chloride) (PVC) releases HCl. Hydrogen Chloride generation begins at temperatures as low as  $130^\circ C$ . Up to 99% of the chlorine contained in PVC is lost as HCl, with very little vinyl chloride monomer formed. In inert atmospheres, and at temperatures ranging from 160 to  $700^\circ C$ , more than 75 pyrolysis degradation products have been identified and they included olefinic hydrocarbons, benzene, toluene, xylenes, ethylbenzenes, aliphatic, naphthalenes, and methylated species. Sometimes condensed aromatics such as biphenyl and anthracene were also identified (13). Although many products have been identified, the major products of PVC pyrolysis were hydrogen chloride gas and benzene. In some cases, chlorinated compounds were also identified at higher temperatures; for example, ethylene chloride at  $400^\circ C$ , chlorobenzene, di- and trichlorobenzenes at  $500-700^\circ C$ , and vinyl and ethyl chloride at  $550^\circ C$  (14). For these reasons, we believe that HCL should have been produced in our RDF pyrolyses.

Degradation of polyethylene (PE) under varying oxidative conditions ( $500-800^\circ C$ ) has also long been carried out. The products identified consisting of olefin and n-hydrocarbon with chain lengths of 8 to 23 carbons, in addition to lower molecular weight species such as acetaldehyde, acrolein and benzene (15). It was found that when oxygen in the gas stream was reduced, the amount of carbon dioxide product decreased and hydrocarbon production increased (16). These findings are consistent with our RDF pyrolyses in that (recall no oxygen is present) few hydrocarbons and relatively more condensable volatiles are in the product slates, consistent with the degradation of plastic components. Our carbon dioxide concentration is greater than from pure plastic degradation, attributable to the cellulose decarboxylation from the paper fraction in RDF.

Since HCl is highly soluble in water, HCl gas produced from pyrolysis of PVC is believed to be trapped in the cold tar trap in the form of hydrochloric acid. The trap tar sample collected was analyzed for water and low molecular weight tar components such as Methanol, Acetaldehyde, Acetone, and Acetic acid, by GC using a Supelco 80/100 mesh Porapak Q column. Using the same column, the

response to HCl was calibrated. Calibration results show that the retention time of HCl is 0.71 minute and therefore does not interfere in a major way with any other peak, but that the Porapak Q column is not sensitive enough to detect HCl unless it has a concentration of at least  $3.65 \times 10^{-6}$  g/ $\mu$ l in our sample. Due to this low HCl sensitivity, we detected no HCl in all our pyrolysis product samples. The HCl analysis is currently in progress.

#### ACKNOWLEDGMENTS

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**Table 1**

MSW Composition, wt % (Analyses from 10 studies)

	Average	standard deviation
MSW Fraction:		
1. Paper	40.1	6.6
2. Yard Waste	13.7	5.1
3. Food Waste	11.5	4.7
4. Wood	3.1	1.1
5. Plastics	4.9	3.4
6. Rubber & leather	1.9	0.9
7. Textiles	2.1	0.8
Subtotal	77.3	2.5
8. Metal	9.5	1.7
9. Glass	9.9	1.6
10. Misc. Inorganics	3.3	2.6
Total	100.0	
Moisture Content	25.6	3.1

**Table 2**

Experimental Conditions Studied

Process variables	Symbol	Range		Comments
Heat flux	q	$12.6 \times 10^{-4}$	to	$21.0 \times 10^{-4}$ W/m <sup>2</sup>
Moisture content	MC	5.0%	to	30.0% dry basis
Particle thickness	L	1.0	to	2.0 cm
Composition variables				
Paper	X <sub>1</sub>	0.57	to	0.95 weight fraction
Plastics	X <sub>2</sub>	0.00	to	0.20 weight fraction
Metal/Glass	X <sub>3</sub>	0.05	to	0.15 weight fraction
Binder	X <sub>4</sub>	0.00	to	0.08 weight fraction

Table 3

Replicate Runs: Reaction Conditions and Integrated Gas Yields over Pyrolysis Time

	Replicates:		difference	fractional difference of Run 24
	Run 24	Run 25		
X1(PAPER)	0.76	0.76	0	
X2(PLASTICS)	0.1	0.1	0	
X3(MET&GLASS)	0.1	0.1	0	
X4(Binder)	0.04	0.04	0	
Q(cal/cm2-s)	4	4	0	
MC(%)	17.5	17.5	0	
L(CM)	1.5	1.5	0	
GAS(%)2	5.473	4.454	1.0187	19.0%
CO(%)2	1.746	1.313	0.4322	25.0%
CO2(%)2	3.135	2.830	0.3044	10.0%
CH4(%)2	0.245	0.183	0.0621	25.0%
C2H2(%)2	0.012	0.010	0.0017	14.0%
C2H4(%)2	0.058	0.050	0.0081	14.0%
C2H6(%)2	0.053	0.068	-0.015	-29.0%
			average:	19.0%

Table 4

Integrated Gas Yields over Pyrolysis Time for  
Comparison Experiments: High Versus Low Plastics Content

	Hi/lo plastics comparison for experiments with high binder, low metal/glass content, and 2 cm thick				Hi/lo plastics comparison for experiments with low binder, high metal/glass content, and 2 cm thick				Hi/lo plastics comparison for experiments with high binder, low metal/glass content, and 1 cm thick			
	Run 18	Run 51	18-51	18-51 /51	Run 33	Run 21	33-21	33-21 /21	Run 54	Run 55	54-55	54-55 /55
X1(PA)	0.71	0.82	-0.102		0.70	0.81	-0.102		0.71	0.82	-0.102	
X2(PL)	0.15	0.05	0.102		0.15	0.05	0.102		0.15	0.05	0.102	
X3(M&G)	0.07	0.07	0		0.13	0.13	0		0.07	0.07	0	
X4(BI)	0.06	0.06	0		0.02	0.02	0		0.06	0.06	0	
Q	5	5	0		5	5	0		5	5	0	
MC(%)	5	5	0		5	5	0		5	5	0	
L(CM)	2	2	0		2	2	0		1	1	0	
GAS(%)2	6.91	7.83	-0.92	-12.0%	5.85	8.42	-2.58	-31.0%	10.66	12.27	-1.60	-13.0%
CO(%)2	1.62	1.88	-0.26	-14.0%	1.62	2.61	-1.00	-38.0%	2.36	2.92	-0.56	-19.0%
CO2(%)2	4.63	5.56	-0.93	-17.0%	3.36	5.12	-1.76	-34.0%	7.69	8.74	-1.05	-12.0%
CH4(%)2	0.31	0.21	0.09	45.0%	0.20	0.36	-0.17	-46.0%	0.32	0.41	-0.09	-21.0%
C2H2(%)2	0.01	0.01	-0.002	-20.0%	0.02	0.02	0.003	20.0%	0.02	0.01	0.01	56.0%
C2H4(%)2	0.16	0.05	0.11	238.0%	0.05	0.10	-0.05	-52.0%	0.09	0.09	-0.001	-1.0%
C2H6(%)2	0.12	0.09	0.03	30.0%	0.10	0.07	0.03	37.0%	0.18	0.07	0.11	161.0%

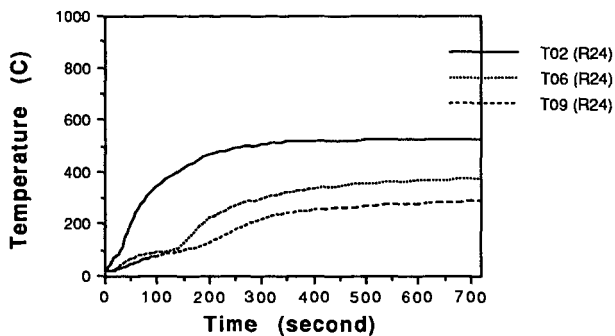


Fig. 1 - Time-Temperature Profiles at 3 different depths from the heated surface (average composition and reaction conditions, centerpoint of range studied, Run 24, conditions shown Table 3)

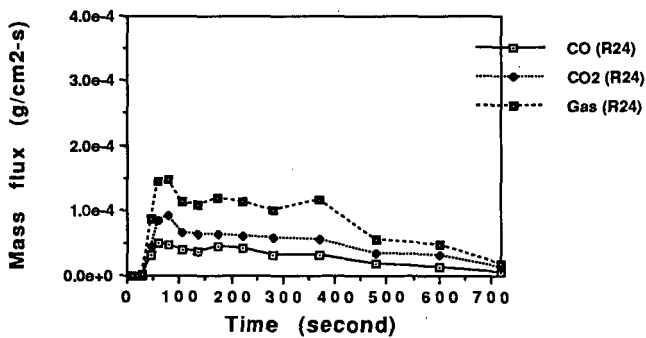


Fig. 2 - Gas Release Histories (Run 24) for Experimental Conditions shown in Table 3

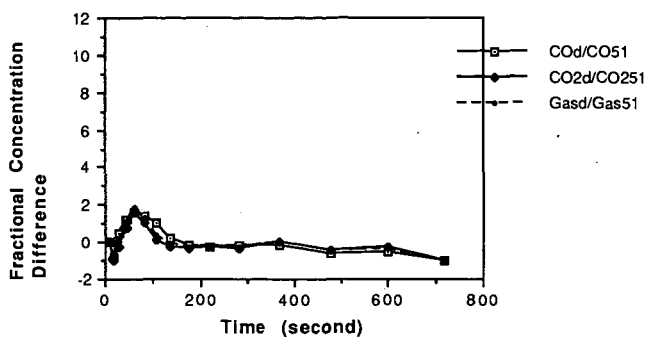


Fig. 3 - Difference in Carbon Oxide and Total Gas Concentration between two direct comparison Runs (Runs 18 and 51) - Normalized by Concentrations in Run 51 (low plastics content)

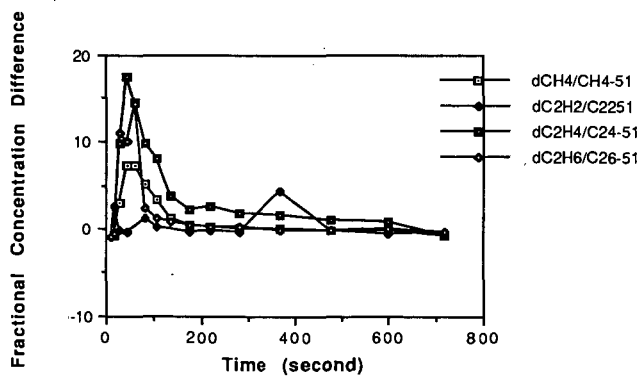


Fig. 4 - Difference in Hydrocarbon Gas Concentration between two direct comparison Runs (Runs 18 and 51) - Normalized by Concentrations in Run 51 (low plastics content)